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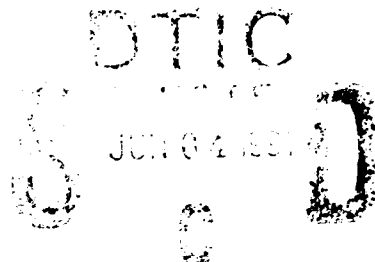
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Technical Report No. 6

Extension of Branches for Orthogonally Fused Molecular Switches

by

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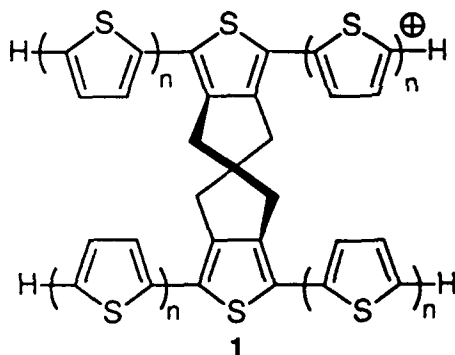
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| <p>Described is the synthesis of two spiro core segments of orthogonally arranged conducting systems. The final systems are to have a potentially conducting chain fused perpendicularly to a second potentially conducting chain via a sigma bonded network. These systems may be suitable for incorporation into future molecular electronic devices. One of the core segments synthesized is based on a thiophene conducting group and it is formed by a zirconium-promoted bis(bicyclization) of bis(diyne) systems. The second is a phenylene-based system which is derived from fluorene. Terminal bromide groups provide the linkage points for further extensions of the chains via palladium-catalyzed cross coupling methods.</p> | | | | | |
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EXTENSION OF BRANCHES FOR ORTHOGONALLY FUSED MOLECULAR SWITCHES

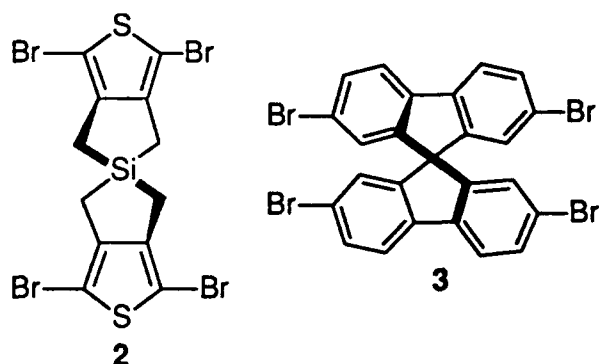
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Since the time of the first room-filling computers, there has been a tremendous drive to compress the size of computing instruments. In order to bring this desire to its extreme, it was conceived that one may be able to construct single molecules that could each function as a self-contained electronic device.² Recently, Aviram of the IBM Corporation suggested that molecules which contain a pro-conducting (non-doped or non-oxidized system, hence insulating) polymer which is fixed at a 90° angle via a non-conjugated sigma bonded network to a conducting (doped or oxidized system) should exhibit properties which would make it suitable for interconnection into future molecular electronic devices. These devices may be useful for the memory, logic, and amplification computing systems.³ The molecule **1** (in doped form) is an example of this pro-conducting/sigma/conducting type of molecule.

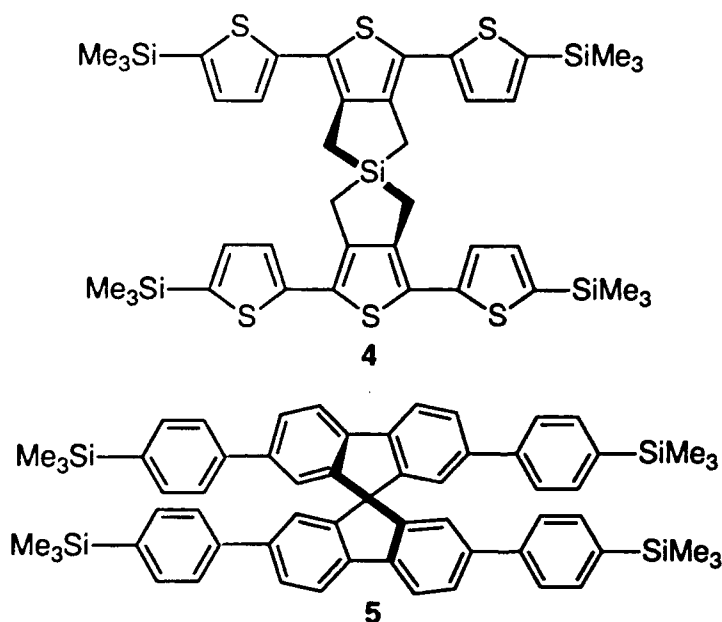


From the synthetic standpoint, there are several features of this class of molecules that require strict architectural attention. First, there must be one spiro-fused junction separating two potentially conducting chains with a tetrahedral bonding atom at the center to maintain the 90° angle via a σ -bonded network. Secondly, all four conducting chains originating from the central segment must be *identical* in length. These requirements prohibit the use of any random polymerization methods. Initial reports suggested conducting chains ~50 Å long (from end to end rather than from end to core) would fulfill the model.³

We recently described an extremely facile approach to the core of two molecules which fit the general class of systems necessary for this electronic model.⁴ The thiophene-based core (2) was synthesized in three steps and the phenylene-based core (3) was prepared in four synthetic step.

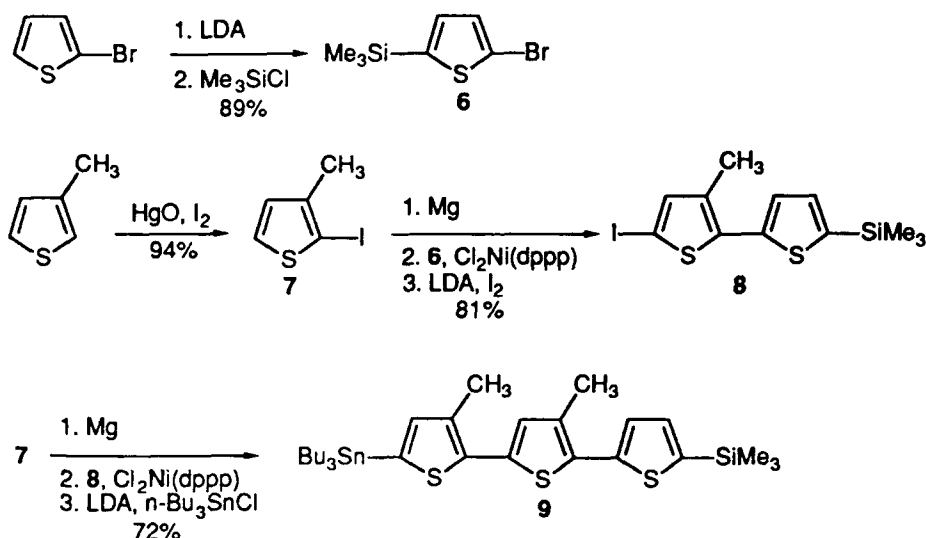


The key to our approach lies in the convergent nature of the synthesis. Namely, the cores **2** and **3** were synthesized independent of the four branching arms. In a single operation, all four branches can be attached to afford the final targets. We previously described the attachment of thiophene and phenylene monomer units to **2** and **3** to yield the extended systems **4** and **5**, respectively.⁴



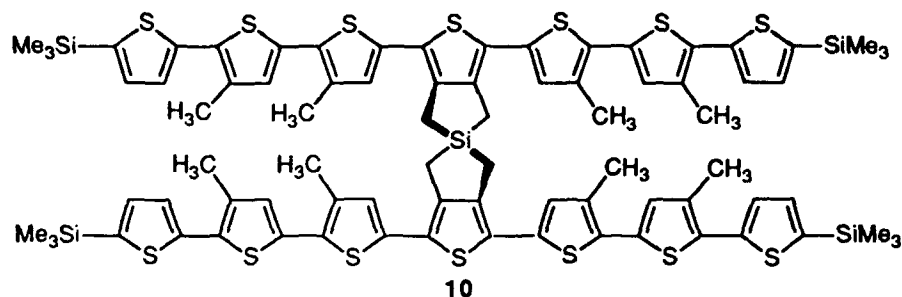
Here we demonstrate that our approach is indeed applicable to the adhesion of larger branching units to the core systems. Furthermore, we show that the cores can be elongated, in a one pot operation, to 23 Å in length (from end to end), approximately half of the final target system.

A functionalized thiophene trimer was synthesized as shown below.



2-Bromothiophene was lithiated with lithium diisopropylamide (LDA) and quenched with chlorotrimethylsilane to give **6**. 3-Methylthiophene was iodinated exclusively at the 2-position with mercury(II) oxide and iodine to give **7**⁵ which was then converted to its Grignard reagent. Treatment of the Grignard reagent of **7** with the bromide **6** and (diphenylphosphino)propanenickel(II) dichloride catalysis⁶ afforded the dimer which was deprotonated with LDA and quenched with iodine to give the dimer iodide **8**. Treatment of the Grignard reagent of **7** with **8** under nickel-catalyzed conditions afforded the trimer which was metalated to give **9** in 72% yield for the final three steps (based on recovered **8**). When the silylated thiophene unit in **9** had a methyl substituent in the position α to silicon, desilylation was extremely facile, even upon silica gel chromatography. This desilylation also occurred with a triethylsilyl group in place of the trimethyl substituent. Thus, we chose to keep the terminal thiophene unit de-alkylated. Note that alkylation of several of the thiophene units was essential in order to maintain a soluble orthogonally fused system as describe below.

With the trimer **9** in hand, we could then address the final coupling reaction. Treatment of the core **2** with excess **9** in the presence of tetrakis(triphenylphosphine)palladium(0) catalyst⁷ afforded the target orthogonal system **10** that is approximately 23 Å in length from end to end, one half of the length necessary to fulfill the Aviram model.



In summary, we describe a convergent approach to the orthogonally fused macromolecules that may function as molecular-sized components in future computing devices.

Spectral Data for Compound 10

IR (KBr) 2950, 1132, 991, 839 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.19 (1/2 ABq, $J = 2.5$ Hz, 4 H), 7.15 (1/2 ABq, $J = 2.5$ Hz, 4 H), 6.99 (s, 4 H), 6.93 (s, 4 H), 2.40 (s, 12 H), 2.37 (s, 12 H), 2.33 (s, 8 H), 0.31 (s, 36 H). ^{13}C NMR (125 MHz, CDCl_3) δ 141.94, 141.22, 140.61, 134.82, 134.80, 134.60, 134.58, 134.25, 131.34, 130.78, 129.60, 128.64, 128.44, 126.77, 17.08, 16.12, 16.00, 0.31. FAB/MS Calc'd maximum isotopic intensity peak for $\text{C}_{80}\text{H}_{84}\text{S}_{14}\text{Si}_5$: 1634. Found: 1634.

Acknowledgements

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